

An innovative dual fuel cell to capture and collect pure NO_x from flue gases

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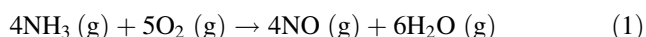
Abstract Nitrogen monoxide (NO), a major air pollutant, can be directly used as a precursor for nitrogen fertilizer production as long as it is collected in a pure form. In this study, an innovative dual fuel cell system was designed for the efficient capture and collection of pure NO_x from industrial flue gases as well as for electricity generation. The system consisted of a methanol/ferric-EDTA fuel cell for NO_x capture and a ferrous-EDTA–NO/air fuel cell for captured NO_x collection. In a separation operation, the maximum power densities, which were obtained at pH 2 and 20 °C, were 785 and 1,840 mW m^{−2} in FC1 and FC2, respectively, and increased with temperature. The highest overall outputs from FC1 and FC2 were measured at pH 2, a result that is possibly attributable to the redox potential difference between the anolyte and catholyte in the fuel cells. In the combined operation, ferrous-EDTA–NO prepared in the cathode compartment of FC1 was successfully and efficiently converted to ferric-EDTA and NO in the anode compartment of FC2. The present approach was considered advantageous for advanced NO_x reuse technology in the respect that valuable products, such as fertilizer, could be produced.

Keywords Dual fuel cell system · Ferrous-EDTA–NO · NO_x reuse · Ferric catholyte · Metal chelate · Selective absorption

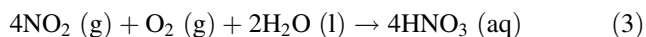
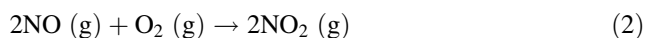
1 Introduction

NO_x, mainly emitted from flue gases [1], is the major cause of acid rain and the depletion of the ozone layer [2, 3], and thus, prevention of its emission is of prime importance. While several treatment technologies based on chemical and biological reactions have been developed to date [4–7], all of them have fatal drawbacks such as a slow aqueous solubility of NO, difficulty in absorbent regeneration, and generation of unwanted byproducts [8–10]. These drawbacks hamper the economic removal of NO_x from flue gases.

A promising and more economically feasible approach is to capture and then reutilize NO_x rather than to simply remove it. In fact, nitric oxide (NO) is involved in the industrial production of nitric acid as a sole intermediate. In this process, which is known as the Oswald process, ammonia is first oxidized to NO with oxygen in the presence of metal catalysts with heating (Eq. 1).



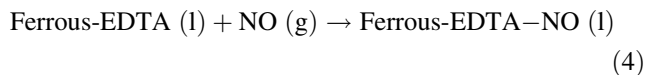
This intermediate is further oxidized to nitrogen dioxide (NO₂) (Eq. 2), which is then combined with water and oxygen, and finally converted to nitric acid (Eq. 3).



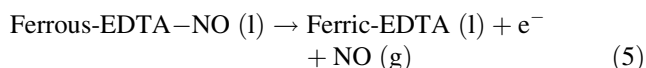
This commercial process, however, is rather costly, as it uses ammonia. If NO is selectively and purely captured from flue gases and then reused for this purpose, the production cost of nitric acid will be greatly reduced; net positive profit may even be possible under well-optimized conditions. The ultimate goal of this study is, therefore, to develop an innovative technology that makes it possible to capture and collect pure NO from flue gases.

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It is well documented that ferrous-EDTA (ethylenediaminetetraacetate) substantially increases the aqueous solubility of NO by the formation of a ferrous-EDTA–NO complex (Eq. 4).



When NO-containing flue gas passes through a ferrous-EDTA solution, only NO remains in the solution, with all the other gases being released. This approach, however, has a critical drawback: the oxidized form of the sorbent, ferric-EDTA, which is continually produced by oxygen contained in flue gases, has greatly reduced sorption capacity toward NO (Eq. 5).



A possible key to improving the viability of this approach is regeneration of the sorption agent ferrous-EDTA. One plausible method for this is to exploit microbial activity, such as in a BioDeNO_x system that takes advantage of denitrifiers and ion-reducing bacteria (IRB) [7–10]. In this system, NO is treated by denitrifiers and ferric-EDTA is reduced to ferrous-EDTA by IRBs. This seemingly implementable technology, however, has the critical problem that the regeneration rate is not fast enough. A substantially faster alternative with added benefits is, thus, required. The primary goal of this study, therefore, is to develop a highly efficient technology for continual sorbent regeneration. To this end, fuel cell technology was employed, on the basis of the high electrochemical reactivity of ferrous- and ferric-EDTA. It has been reported that the reduction of ferric-EDTA was successfully achieved in a microbial fuel cell (MFC) [11]. In this novel MFC, ferric-EDTA serves as a terminal electron acceptor (TEA) in the cathode while being reduced to ferrous-EDTA during the MFC operation. We constructed a fuel cell in a very similar manner. The only difference was the replacement of the microbial anode component with a direct methanol fuel cell for successful NO_x capture, according to an enhanced regeneration rate. In addition, for continuous operation, a ferrous fuel cell using ferrous-EDTA (or NO-captured ferrous-EDTA) as a fuel [11] was also designed. In this second type of fuel cell, ferrous-EDTA–NO is oxidized to ferric-EDTA on the anode electrode, thereby producing electricity. In this manner, NO gas can be collected in a pure form, which can be chemically converted into high value products such as nitrogen fertilizers, thereby reducing the overall NO_x treatment cost.

2 Experimental details

A dual fuel cell system was constructed by combining two fuel cell units, a methanol fuel cell (FC1) with ferric-EDTA

as a TEA and a ferrous-EDTA fuel cell (FC2) (Fig. 1). FC1 uses methanol as an anodic fuel, and ferric-EDTA in the cathodic chamber is converted into ferrous-EDTA, which is used for NO capture from mixed gases. In the FC2 unit, ferrous-EDTA with NO (ferrous-EDTA–NO) is oxidized and releases NO. The released NO is then collected. The volume of each compartment of both fuel cells is 120 mL. All electrodes are made of carbon cloth (Type A, E-TEK, 15 cm² projected surface area) and commercial Pt/C (E-Tek, 20 wt%, 2 mg cm^{−2}) and Pt/Ru (E-Tek, 20 wt%, 2 mg cm^{−2}) are used for methanol oxidation and oxygen reduction in FC1 and FC2, respectively. A mixed gas, consisting of 1 % NO and 99 % N₂, is first injected into the cathode compartment in FC1 where electrochemical reduction is supposed to occur, and thus, NO is captured upon the formation of ferrous-EDTA from ferric-EDTA. The resultant product (i.e., ferrous-EDTA–NO) is moved to the anode compartment in FC2, and pure NO is collected while ferrous-EDTA is converted to ferric-EDTA. This cycle is repeated. Cell voltage and maximum power density with varied pH and temperature were measured using a digital multimeter (Keithley 2700, USA) and electrochemical workstation (CHI604C, USA). The concentration of iron-EDTA was varied from 10 to 100 mM, and the cell was operated at 20, 40, 60, and 80 °C, respectively. Ferric-EDTA and ferrous-EDTA–NO complex were prepared according to Li et al. [12] with minor modifications. For the preparation of ferrous-EDTA–NO, FeSO₄ instead of FeCl₂ was used and the pH of the solution was adjusted to 7.0 with 0.5 M NaOH before NO absorption tests. The concentration of ferrous-EDTA–NO was determined from a calibration curve of the absorbance (420 nm) to the concentration of ferrous-EDTA–NO. The absorbance was directly determined by a UV-2000 spectrophotometer (UNICO Shanghai Instruments Co., Ltd.) [13]. The concentrations of ferrous ions and total iron in the solution were determined by the 1,10-phenanthroline-colorimetry method at 510 nm with a spectrophotometer [14].

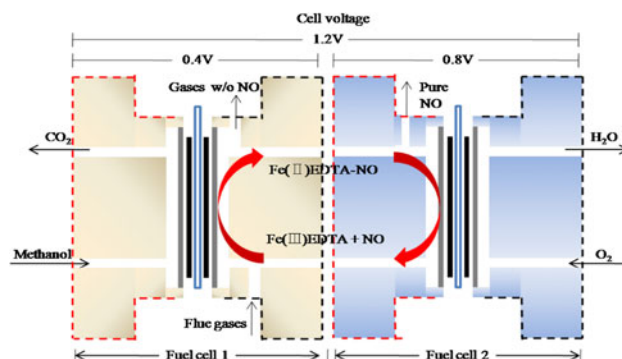


Fig. 1 Dual fuel cell system

Fig. 2 FC1 operation; cell voltage, Fe^{2+} /total iron, and maximum power density along with time (anolyte: 1 M methanol, catholyte: 10 mM ferric-EDTA (pH 1.3), operating temperature: 20 °C, external resistance: 1,000 Ω)

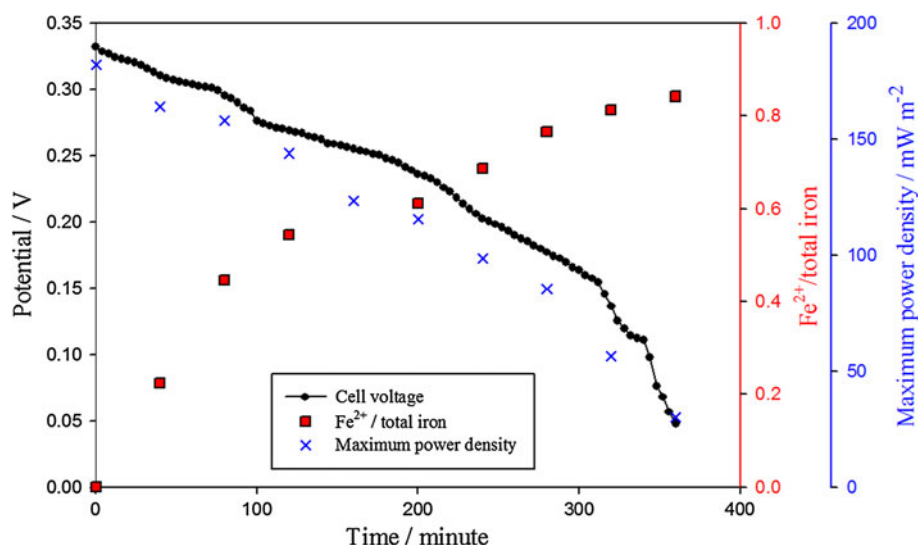
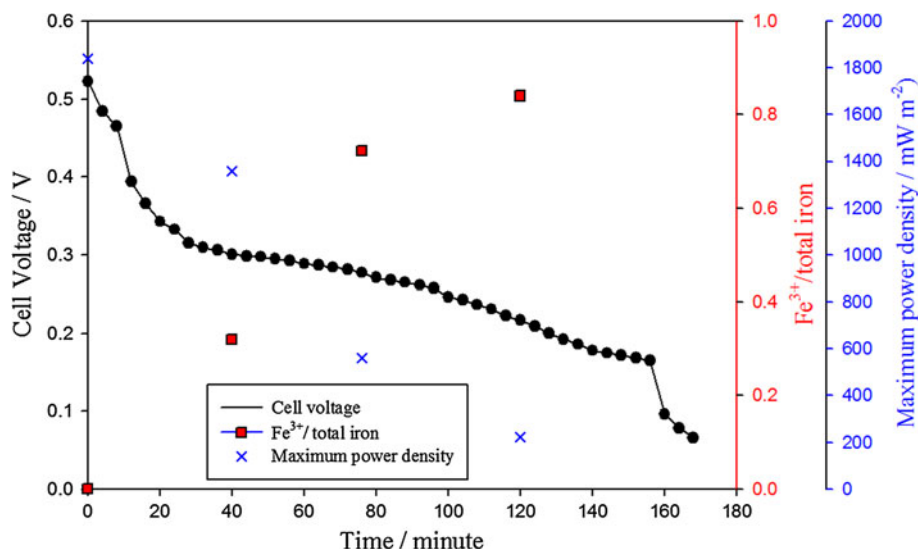


Fig. 3 FC2 (w/o NO) operation; cell voltage, Fe^{3+} /total iron, and maximum power density along with time (anolyte: 10 mM ferrous-EDTA (pH 2.4), operating temperature: 20 °C, external resistance: 1,000 Ω)



3 Data and results

3.1 Performance of each fuel cell

To ascertain if each fuel cell functioned properly, FC1 and FC2 were operated separately at a fixed external circuit resistance (1,000 Ω) and at 20 °C. For FC1 operation, 250 mL of 1 M methanol and 10 mM ferric-EDTA solutions were used as an anolyte and catholyte, respectively, and were circulated from an outside reservoir to each chamber at a rate of 50 mL min⁻¹ using a plastic pump for effective mixing. At an external resistance of 1,000 Ω , a value of approximately 0.33 V was measured at the initial state in the methanol/ferric-EDTA fuel cell and the voltage thereafter dropped gradually to approximately 0.05 V after 6 h (Fig. 2). Power densities were measured at intervals of

40 min and decreased from an initial value of roughly 785–50 mW m⁻² (Fig. 2). During the cell operation, more than 80 % of the ferric-EDTA was transformed to ferrous-EDTA within 6 h in the cathode compartment, indicating that the regeneration of the key agent, i.e., ferrous-EDTA with exceptionally high sorption ability toward NO, could be achieved rapidly. Considering that iron-reducing microbes require much more time (e.g., more than 24 h) for regenerating ferrous-EDTA in the case of an existing BioDeNO_x device [15, 16], this result is quite promising.

Before testing the NO capturing process (i.e., ferrous-EDTA + NO → ferrous-EDTA–NO), FC1 was separately operated without NO at an external resistance of 1,000 Ω and 20 °C. The cell voltage initially reached a maximum of 0.53 V and then rapidly dropped to 0.3 V in 30 min, decreased slowly over the next 2 h, and finally dropped

quickly (Fig. 3). The highest maximum power density was measured at the initial state ($1,820 \text{ mW m}^{-2}$), and it decreased gradually along with a cell voltage drop. This result was used as a positive control to compare the efficiency with that obtained from the fuel cell using a ferrous-EDTA–NO anolyte. To enhance the cell performance, the fuel cell was operated under different pH and temperature conditions (Fig. 4). A slight increase of cell voltages was observed with increased temperature in both fuel cells,

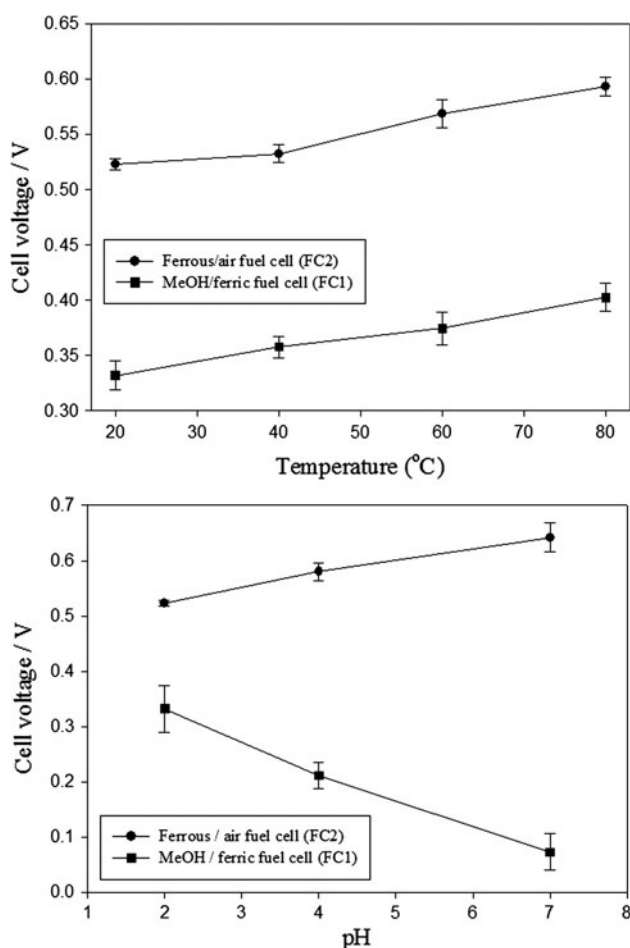


Fig. 4 Effect of different temperature and pH conditions of iron-EDTA on fuel cell performance (0.5 M methanol, 10 mM ferric-EDTA, 10 mM ferrous-EDTA, external resistance: 1,000 Ω)

which is possibly attributable to the electrochemically enhanced catalytic activity. While the cell voltage measured in the methanol/ferric-EDTA fuel cell decreased with a pH increase, it slightly increased in the ferrous-EDTA/air fuel cell. This result can be explained by the redox potential existing between the anolyte and catholyte. It is known that the redox potential between ferrous- and ferric-EDTA couples is 0.5 V versus SHE (standard hydrogen electrode) at pH 2.0. Since the increased pH caused a decrease of the redox potential, the cell voltage produced by coupling the methanol/ CO_2 (0.03 V vs. SHE) half reaction and ferric/ferrous-EDTA half reaction was decreased in FC1, but that from ferrous-EDTA/ferric-EDTA and $\text{O}_2/\text{H}_2\text{O}$ (1.23 V vs. SHE) half reactions was increased in FC2. As a TEA, this decreased redox potential has a disadvantage of reduced power output in FC1, but offers an advantage of increased power output in FC2. Therefore, pH 2 appeared to be an optimal condition since the total voltage production, which is the sum of the voltages from both cells, was the highest (about 0.85 V) at this point.

3.2 Combined fuel cell system

The main purpose of this study was to construct a semi-continuous fuel cell system to capture and collect pure NO_x from mixed gases; thus, FC1 and FC2 were combined and operated. After FC1 operation with 10 mM ferric-EDTA as a catholyte at 20 $^\circ\text{C}$ for 4 h, the color of the solution changed from orange, indicating ferric-EDTA, to light green, indicative of ferrous-EDTA (Fig. 5). Approximately 90 % of the ferric-EDTA was reduced to ferrous-EDTA at this point. NO capture was then attempted by purging a mixed gas consisting of 1 % NO and 99 % N_2 for 5 min. With the addition of NO, the color of the catholyte changed to black (Fig. 5), indicating the formation of a ferrous-EDTA–NO complex. This complex solution was then used as an anolyte for the operation of FC2. This was carried out at 60 $^\circ\text{C}$ to roughly mimic industrial flue gases. The results obtained using ferrous-EDTA–NO were quite similar to those from FC2 with ferrous-EDTA in terms of cell voltage, power density, and iron ion concentration (Fig. 6). This result indicated that the existence of NO did not affect

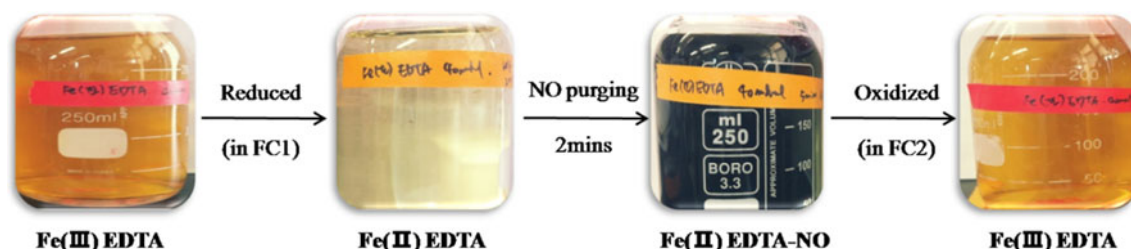


Fig. 5 Color change during ferric-EDTA reduction, ferrous-EDTA–NO formation, and ferrous-EDTA–NO oxidation

Fig. 6 FC2 (with NO) operation; cell voltage, Fe^{3+} /total iron, and maximum power density along with time (anolyte: 9 mM ferrous-EDTA-NO +1 mM ferric-EDTA (pH 2.2), operating temperature: 60 °C, external resistance: 1,000 Ω)

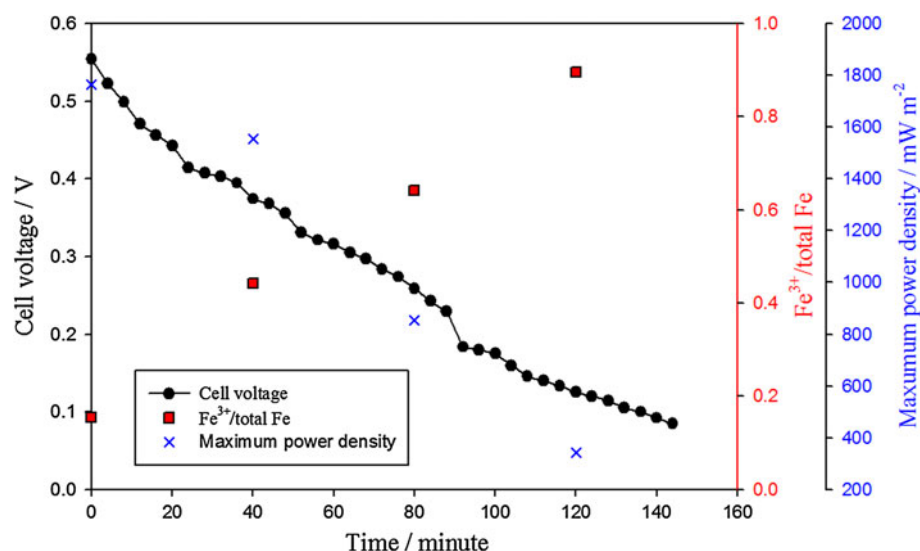
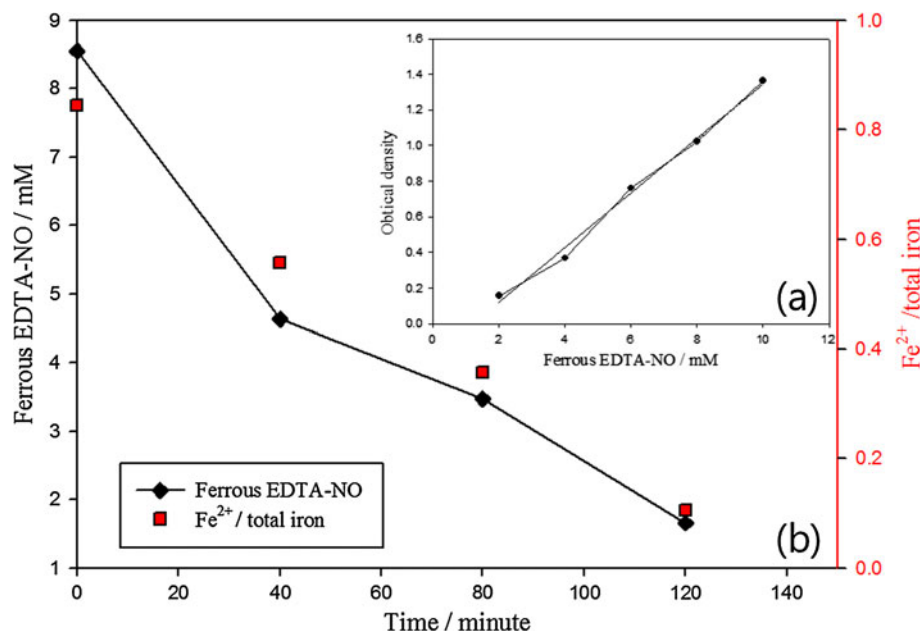


Fig. 7 The effect of ferrous-EDTA-NO concentration and Fe^{2+} /total ion ratio on fuel cell operation time



the fuel cell performance, and thus, ferrous-EDTA-NO as well as ferrous-EDTA could be used as a fuel. Figure 6 shows the effects of ferrous-EDTA-NO concentration on the fuel cell operation time. With a standard curve of the correlation between optical density and ferrous-EDTA-NO concentration, it was possible to estimate the ferrous-EDTA-NO concentration by simply measuring the optical density (Fig. 6a). A gradual decrease in the amount of ferrous-EDTA-NO (from the initial 8.6 to 2 mM) was observed within 2 h (Fig 7b). The ratio of ferrous ion to total iron also displayed a similar trend, indicating that the oxidation of ferrous-EDTA-NO was successfully achieved. This was also supported by the color change from black-brown ferrous-EDTA-NO to orange-brown ferric-EDTA (Fig. 4).

4 Conclusions

In this study, a novel dual fuel cell system that can selectively capture and collect NO from flue gases was constructed, and its potential applicability was demonstrated. This innovative system enables NO from flue gases to be captured and collected, with an added benefit of electricity generation, suggesting high potential for field application. The collected pure NO can be used as feedstock for the production of nitric acid (and nitrogen fertilizer), as in the case of Oswald's method.

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